

# **Combustion Properties of Lignin Residue from Lignocellulose Fermentation**

Prepared for  
National Renewable Energy Laboratory  
NREL Subcontract ACG-8-18021-01

Prepared by  
S.L. Blunk  
B.M. Jenkins

Department of Biological and Agricultural Engineering  
University of California  
Davis, California, USA 95616

April 2000

# **Combustion Properties of Lignin Residue from Lignocellulose Fermentation**

## **Abstract**

Fermentation of lignocellulosic biomass produces a lignin rich residue. This residue is frequently proposed as fuel for steam and power generation to support the operations of the fermentation facility and for export power. The purpose of this research was to determine the combustion properties of lignin rich residues produced from the fermentation of softwood and hardwood biomass. Specifically, ligneous residues were evaluated for their fouling and slagging tendencies, as well as standard fuel properties. Samples of residue were tested for volatile ash and ash fusibility to assess the potential for slagging in biomass furnaces and boilers and fireside fouling of heat exchangers. Recently developed whole fuel testing procedures were also compared against standard ASTM fusibility procedures. Whole fuel tests generally show initial ash deformation occurring at lower temperatures than the ASTM pyrometric cone method using calcined ash (ASTM D 1875). Hardwood lignin produced greater release of potassium to the gas phase at higher temperatures, likely leading to greater sulfate deposition in boilers. In general, residues appear to be of low to moderate fouling type, but results suggest that materials used during pretreatment and fermentation or their derivatives can carry over into the residue with potentially undesirable consequences for the combustion system.

## **1.0 Introduction**

Lignocellulosic biomass encompasses agricultural wastes, herbaceous wastes, deciduous (hardwood) and coniferous (softwood) trees and municipal solid wastes (MSW). Woody biomass is mainly comprised of cellulose, hemicellulose and lignin. During the fermentation process, including pretreatment, the cellulose and hemicellulose are broken down into sugars and fermented to produce ethanol, while the lignin remains for the most part unchanged. The lignin content of softwoods ranges from about 25%-35%, which is greater than the lignin content of hardwoods, 18%-25%. [1]. The fermentation of both hardwood and softwood material yield residues that are lignin rich and are believed to be good candidates for thermal conversion. [2].

Several studies have utilized ligneous residues as primary fuel sources or co-fired lignin with either natural gas or coal. [3,4]. The purpose of this study was to determine the thermal conversion characteristics for a hardwood and a softwood fermentation residue. In addition to the standard fuel properties, the fouling and slagging tendencies of each residue were explored.

## **2.0 Materials**

### **2.1 Softwood Lignin**

The softwood lignin material was comprised of washed, 2<sup>nd</sup> stage prehydrolysate prepared from a 1<sup>st</sup> stage prehydrolysate blend by pretreating with 0.4% H<sub>2</sub>SO<sub>4</sub> at 215°C for 3 min., in the NREL 4-L steam explosion reactor. The 1<sup>st</sup> stage material was prepared from a large batch designated QLG whole tree waste, which was well blended, barreled and frozen until used.

### **2.2 Hardwood Lignin**

Hardwood yellow poplar (*Liriodendron tulipifera*) sawdust was pretreated in the NREL ethanol pilot plant Sands model CD-300 hydrolyzer. Pretreatment conditions were 200°C, an acid concentration of about 0.35% and a residence time of approximately 5 minutes. The feed rate of sawdust feedstock (47% moisture) into the Sands reactor was approximately 76 kg/h, with a solids level of about 20% in the hydrolyzer. A secondary heat treatment step was used to breakdown oligomers into monomers. Water-washed pretreated solids and conditioned pretreatment liquors were then subjected to simultaneous saccharification and cofermentation (SSCF). Whole slurry was collected after performing a heat kill to inactivate the recombinant microorganisms. After cooling, the inactivated whole slurry residue was separated into wet solids and free liquor fractions. These fractions were stored at -4°C until residue testing could be performed.

## **3.0 Methods and Procedures**

### **3.1 Handling and Drying of Samples**

Both residues were received as partially frozen masses, were thawed, well mixed by hand and oven dried at 100°C to constant weight. The dried samples were stored in airtight plastic bottles until use.

### **3.2 Composition, Density and Heating Value of the Ligneous Residue**

The samples were subjected to a proximate analysis to determine moisture and ash contents, volatile matter, and fixed carbon, according to ASTM E871, D1102 and E872, respectively. Also determined were the higher heating value at constant volume (bomb calorimeter), using ASTM E711/D2015, bulk density (based on ASTM E873 and [5]) and particle size distribution of the dry sample (ASAE S319). Analysis of ultimate composition, elemental composition and water-soluble alkali were performed by an independent laboratory, Hazen Research Incorporated, Golden CO.

The bulk density of each sample was found using a modified drop test based on ASTM E873, where a beaker was filled to a desired volume depending on the amount of sample available, weighed and then dropped 10 times from a height of 10 cm onto a rubber pad. Additional sample was added to the beaker to achieve the initial volume and the density was calculated. For the bulk density and particle distribution analysis for the hardwood lignin sample, residue dried at 40°C was used. During the initial oven drying of the hardwood sample at 100°C, caramelization of the sugars present in the sample was initially thought to have occurred. Experimentally, there was found to be very little difference in the moisture and other properties of the hardwood lignin dried at 40°C and 100°C.

### **3.3 Ash Volatility**

To determine the fractional amounts of ash volatilized at temperatures above 575°C, the samples were heated at a controlled rate (8-15° C/min depending on temperature range) in an air atmosphere muffle furnace, held for 2 h at each temperature, cooled to ambient and weighed to determine the ash fraction. Temperatures used were 575, 750, 900 and 1000°C. The fraction of volatile ash may be related to the fouling potential due the presence of volatile inorganics available for deposition on equipment [6], although the weight loss observed can also be due to the decomposition of hydrates, carbonates, and other species that would not necessarily contribute substantially to fouling.

### **3.4 Ash Fusibility**

Fusibility tests were conducted both on pelleted whole fuel samples, as per [7], and pyrometric cones of fuel ash prepared according to ASTM D1857/E953. The fuel was milled to pass a 20-mesh (841 µm) screen and then used for both tests.

Approximately one gram of pelleted fuel was tested at 50°C increments within the temperature range 800 - 1550°C. Each pellet with refractory support was weighed and placed into the pre-heated Kanthal EPD High Temperature Melting Furnace for a 20-minute duration. The support and remaining fuel residue were removed from the furnace, cooled to ambient in a desiccator and weighed. The final physical characteristics of the remaining pellets were observed and ranked based on the procedure set forth in [7].

For the ASTM pyrometric cone test, the fuel was ashed at 575°C for 2 h. The ash was mixed with a 10% solution of dextrin containing 0.1% salicylic acid, which acts as a binder, and then placed in a lightly lubricated cone shaped mold, as per ASTM D1857/E953. After partial drying, the cones were removed from the mold and placed in a desiccator. Three cones were tested for each residue. The cones were inserted into a Kanthal EPD High Temperature Melting Furnace on indented supports and heated in air at a rate of 10-20°C/min, starting at 800°C, to observe the standard deformation temperatures (Initial deformation, Softening, Hemispherical and Fluid).

### 3.5 SO<sub>2</sub> release

Sulfur dioxide formation was determined by extracting and analyzing gas samples during combustion of lignin pellets in an electrically heated, quartz lined vertical tube furnace. The furnace arrangement is shown schematically in Figure 1. The furnace bore was 75 mm diameter. Furnace temperature was controlled from a thermocouple situated against the wall of the lining at the center of the furnace. Air at a controlled rate ( $3.5 \text{ L min}^{-1}$ ) was admitted through the bottom of the furnace. Pellets of each type of lignin, approximately 1 g dry weight, were placed on a honeycomb ceramic base and suspended at the center of the furnace. The furnace was preheated to a temperature of  $800^\circ\text{C}$  prior to introducing fuel samples. Gas samples were withdrawn from the furnace and analyzed via continuous analyzers for SO<sub>2</sub> and CO<sub>2</sub>. A diluter pump drawing purified air was used to reduce the sample concentration ahead of the analyzers. SO<sub>2</sub> was analyzed by UV absorption (Monitor Labs Model 8500), while CO<sub>2</sub> was analyzed via NDIR (Anarad Model 600). Sample and air flows were measured continuously via rotameter and calibrated against a dry test meter measuring total sample volume. Sample weight was recorded by means of an analytical balance from which the fuel sample and support were suspended.

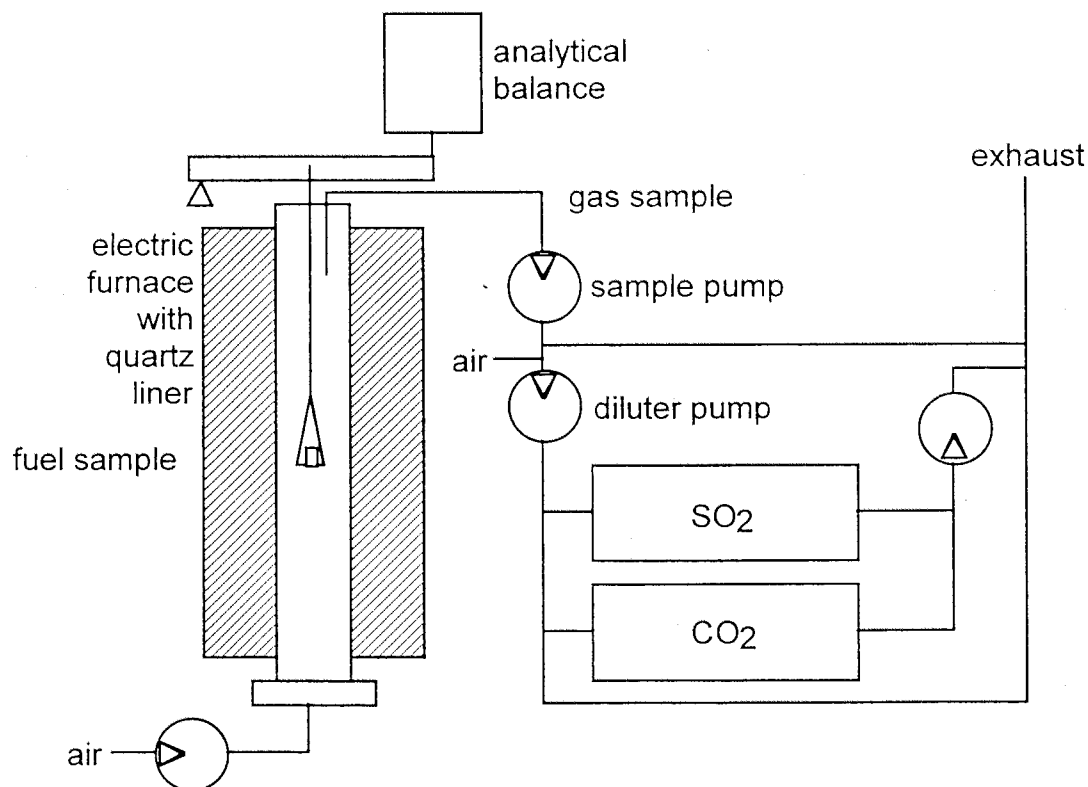


Figure 1. Schematic arrangement of vertical tube furnace and gas sampling equipment.

### **3.6 Microprobe analyses of ash slags**

Glassy slags produced from the lignin fuel ash at the highest Kanthal furnace temperatures were analyzed using a Cameca SX50 electron microprobe. Vertically sectioned samples of each slag were mounted, polished and carbon coated. The microprobe was used to analyze composition of the glassy and mineral phases of the slags, including oxides of Na, Mg, Al, Si, P, S, K, Ca, Ti, and Fe. Back scattered electron (bse) images from the samples were used to investigate the phase structure.

## **4.0 Results**

### **4.1 Properties of Residues**

Compositions of the two lignin samples are listed in Table 1. The samples were subjected to a proximate analysis to determine moisture, ash, volatile matter, and fixed carbon. These values, as well as the higher heating values, HHV, are summarized in Table 2. As-received moisture contents of the residues were 75.3% for the softwood and 72.5% for the hardwood.

Particle size distributions are shown in Table 3 and Figure 2. The fine nature of the lignin is indicated by the 19.7% of mass of the hardwood residue and 24.2% of mass of the softwood residue passing 200 mesh (74  $\mu\text{m}$ ). This fineness of the lignin suggests special handling will be required for the use of the lignin as fuel.

### **4.2 Ash Volatilization**

Relative ash contents from samples heated at 750, 900, and 1000°C were computed from the ash at 575°C. These relative amounts are shown in Figure 3. Although the total ash content for the softwood lignin is small (0.6%), there is about a 30% loss between 575 and 750°C, but little change above 750°C. For the hardwood residue there is little volatile loss, about 5%, over the temperature range. At least part of the weight loss is associated with sulfur volatilization. The limited loss of weight in the hardwood sample is consistent with the greater retention of sulfur in the ash of this fuel at 600°C, and the combined loss of potassium and sulfur at higher temperatures (see below).

**Table 1. Composition of lignin residues.**

Ultimate Analysis	Hardwood Lignin (% dry matter)	Softwood Lignin (% dry matter)
C	51.20	62.17
H	5.70	5.89
N	1.07	0.15
S	0.24	0.06
Cl	0.04	--
Ash	3.40	0.62
O (by difference)	38.39	31.11
Elemental Analysis of Ash *	(% ash)	(% ash)
SiO <sub>2</sub>	16.59	47.02
Al <sub>2</sub> O <sub>3</sub>	3.15	10.18
TiO <sub>2</sub>	0.17	0.41
Fe <sub>2</sub> O <sub>3</sub>	1.68	2.19
CaO	16.90	9.20
MgO	3.33	1.92
Na <sub>2</sub> O	1.40	5.87
K <sub>2</sub> O	25.60	1.90
P <sub>2</sub> O <sub>5</sub>	21.19	<0.01
SO <sub>3</sub>	10.90	11.00
Cl	<0.01	--
CO <sub>2</sub>	0.53	3.37
Total	101.44	93.06
Water Soluble Alkali	(% ash)	(% ash)
Na <sub>2</sub> O	0.198	2.720
K <sub>2</sub> O	12.6	0.197
Alkali Index (kg/GJ)	** 0.202	0.0198

\*Calcined @ 600 C prior to analysis

\*\*Based on HHV, not corrected for S

**Table 2. Properties of lignin residues.**

Parameter	Hardwood Lignin Mean Value	Softwood Lignin Mean Value
Volatile Matter (% db)	74.57	73.14
Fixed Carbon (% db)	22.03	26.24
Bulk Density (kg/m <sup>3</sup> )	123	329
HHV (MJ/kg) (db)	21.45	23.50

**Table 3. Particle size distributions of lignin samples.**

Mesh	Size ( $\mu\text{m}$ )	Hardwood Lignin Mass Fraction (% retained)	Softwood Lignin Mass Fraction (% retained)
10	> 2000	0.00	15.23
14	1410	0.00	--
20	841	17.50	20.62
40	420	26.12	14.78
60	250	16.52	--
100	149	18.00	17.12
200	74	2.18	8.06
Pan	< 74	19.68	24.19
Total		100.00	100.00

-- Not applicable

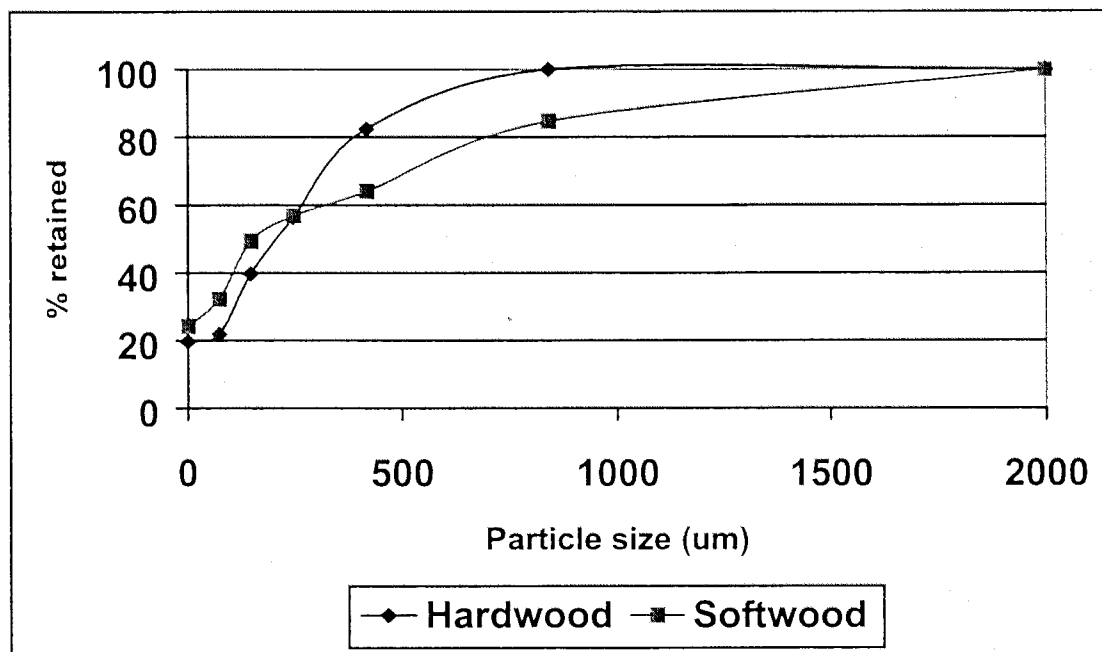


Figure 2. Particle size distributions of dried lignin samples.



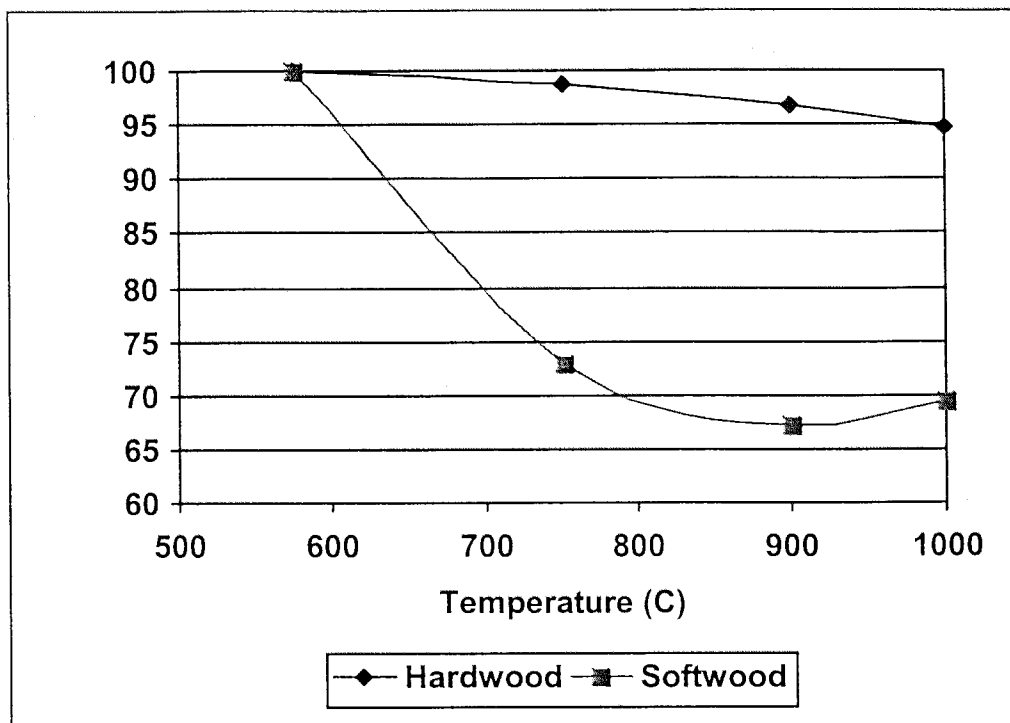


Figure 3. Relative ash contents of lignins at temperatures above 575°C.

### 4.3 Ash Fusibility

Results for the pelleted whole fuel ash fusibility tests conducted according to the criteria set forth by Jenkins, et al. [7] are listed in Table 4. Results for the standard pyrometric cone test conducted according to ASTM D1857/E953 are listed in Table 5.

A comparison of the pyrometric cone results with the whole fuel combustion experiments reveals several differences, especially in the determination of the initial deformation temperature (IT) of the ash. For example, the IT for the ASTM test on softwood is 1120°C, whereas the whole fuel tests indicate liquid formation at temperatures beginning around 950°C, 170°C lower. The two methods differ substantially in the determination of the lower fusion points for the ash. Both methods yield comparable results for the fluid point (Stage 5 in the pellet test and FT in the cone test). The lower IT associated with the pellet test implies a greater fouling potential at normal boiler temperatures than does the cone test.

**Table 4. Whole Fuel Combustion Ash Fusibility for Lignin Residues.**

Stage*	Hardwood Lignin	Softwood Lignin
	Temperature achieved (°C)	Temperature achieved (°C)
1	<900	< 950
2	900	950
3	1050	1050
4	1150	1150
5	1200	1250
6	>1350	1550

Stage 1: No apparent sintering of ash particles in pellet or pellet to refractory support.

Stage 2: Weak sintering of particles in pellet, high porosity, pellet free of refractory support.

Stage 3: Pellet contracted to spherical shape with rough surface texture, particles strongly sintered, low porosity surface, slagged to refractory support.

Stage 4: Pellet contracted to smooth spherical shape, slagged to refractory support.

Stage 5: Ash fully molten with flat shape and thickness less than approximately 2 mm.

Stage 6: Ash vaporized or absorbed by refractory support with no measurable thickness.

\* Criteria for stages given in [6], [7].

**Table 5. ASTM Pyrometric Cone Temperatures for Lignin Residues (oxidizing atmosphere)**

Fusion State	Hardwood Lignin	Softwood Lignin
	Temperature (°C)	Temperature (°C)
Initial Deformation (IT)	1100	1120
Softening (ST)	1200-1220	1190
Hemispherical (HT)	1230-1250	1220
Fluid (FT)	1320-1340	1260

IT: Initial Deformation Temperature; ST: Softening Temperature; HT: Hemispherical Temperature; FT: Fluid Temperature

#### 4.4 SO<sub>2</sub> release

Typical SO<sub>2</sub> and CO<sub>2</sub> release from softwood and hardwood lignins are shown in Figures 4 and 5 respectively. Shown are preliminary concentrations measured at the furnace exit. The hardwood lignin, with its higher sulfur concentration (0.24% sulfur in dry matter), produces a peak SO<sub>2</sub> concentration about 4 times greater than the softwood lignin (0.06% sulfur in dry matter). The peak SO<sub>2</sub> concentration appears some time later than the peak CO<sub>2</sub> concentration. This result is to some extent due to the longer time constant of the SO<sub>2</sub> instrument, but also indicates the sulfur oxidation occurring during the later char burning stages of the sample, evidenced by the slower burning rate after about 50 s as in Figure 6.

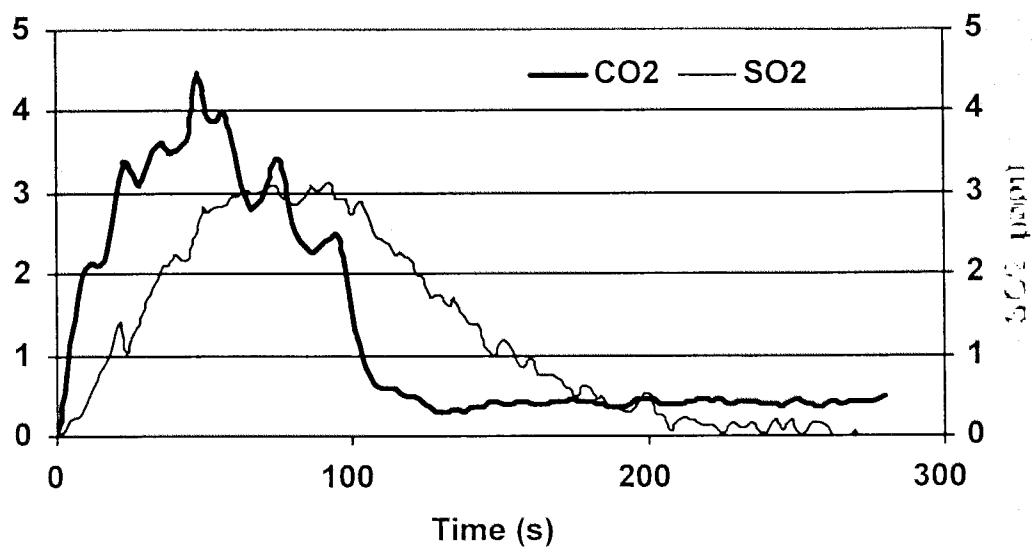


Figure 4. CO<sub>2</sub> and SO<sub>2</sub> release from softwood lignin.

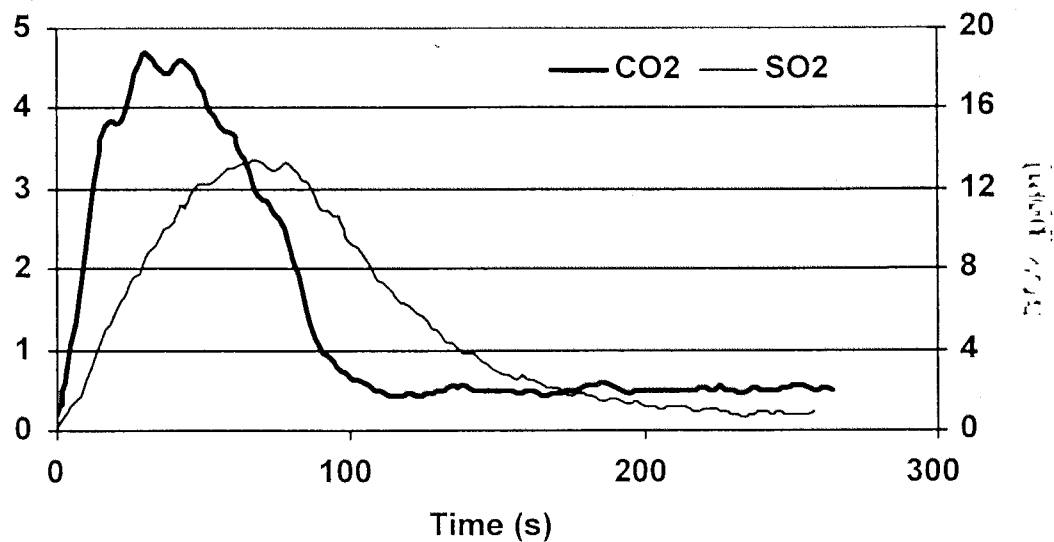


Figure 5. CO<sub>2</sub> and SO<sub>2</sub> release from hardwood lignin.

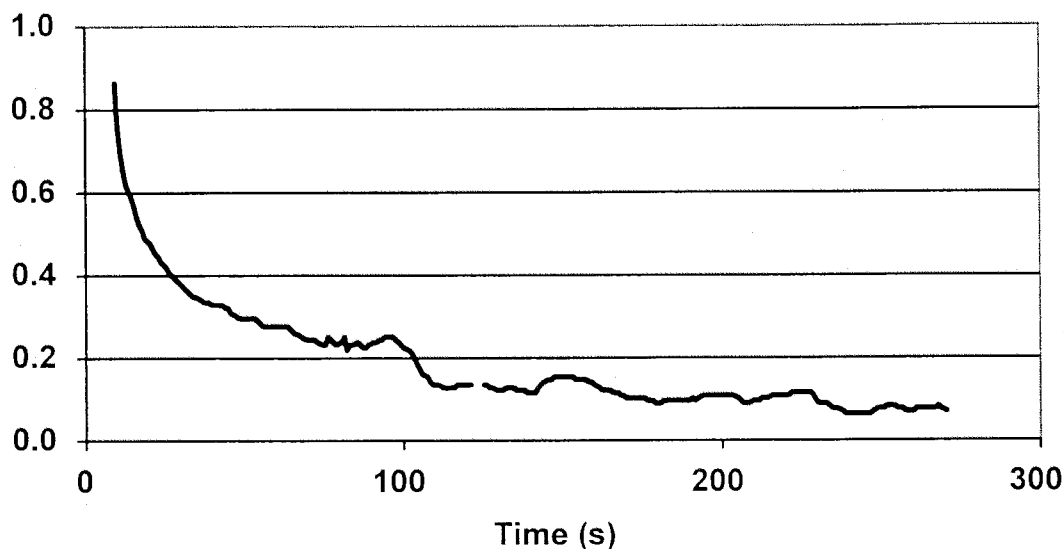


Figure 6. Residual weight fraction for softwood lignin burned in air at 800°C furnace temperature (irregularities in the curve at lower weight fraction are due largely to instabilities in the furnace flow and the consequent effect on the balance measurements).

Sulfur balances reveal that for these tube furnace experiments, more than 60% of the fuel sulfur in softwood lignin is released as  $\text{SO}_2$  into the gas phase, and better than 70% for the hardwood lignin. Further calibrations are still to be conducted to confirm the sulfur release, but these results are largely consistent with the sulfur balances for the results of Table 1 for fuel ashed at 600°C. The softwood lignin ash retains 44% sulfur, while the hardwood lignin retains 62% sulfur at that temperature. The higher temperature associated with tube furnace experiments would be expected to yield higher conversion to  $\text{SO}_2$ .

#### 4.5 Microprobe analyses of lignin ash slag

Backscattered electron images of slags from softwood and hardwood lignin are shown in Figures 7 and 8, respectively. These slags consist of a glass phase in which various inclusions occur. Compositions of the glasses are listed in Table 6. The slag compositions reflect the fuel ash compositions (Table 1). The glass from softwood lignin is a high silica material, and nearly pure silica inclusions are found within the melt (Figure 7). Potassium bearing alumina-silicate inclusions also appear. In contrast, the hardwood lignin produces an

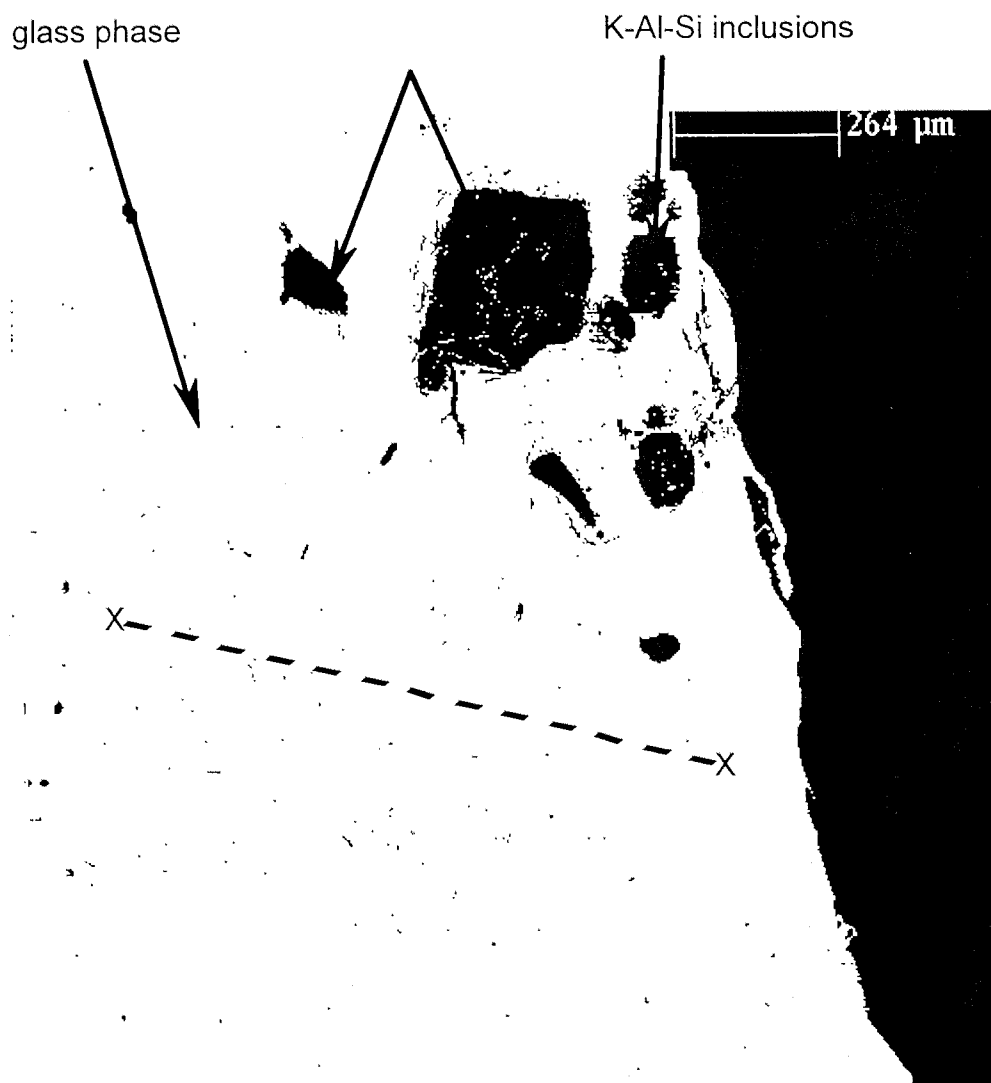


Figure 7. Backscattered electron image of slag from softwood lignin, 63X. Dashed line X---X indicates line along which analyses of glass phase composition were collected. Also shown are silica and potassium-alumina silicate inclusions.

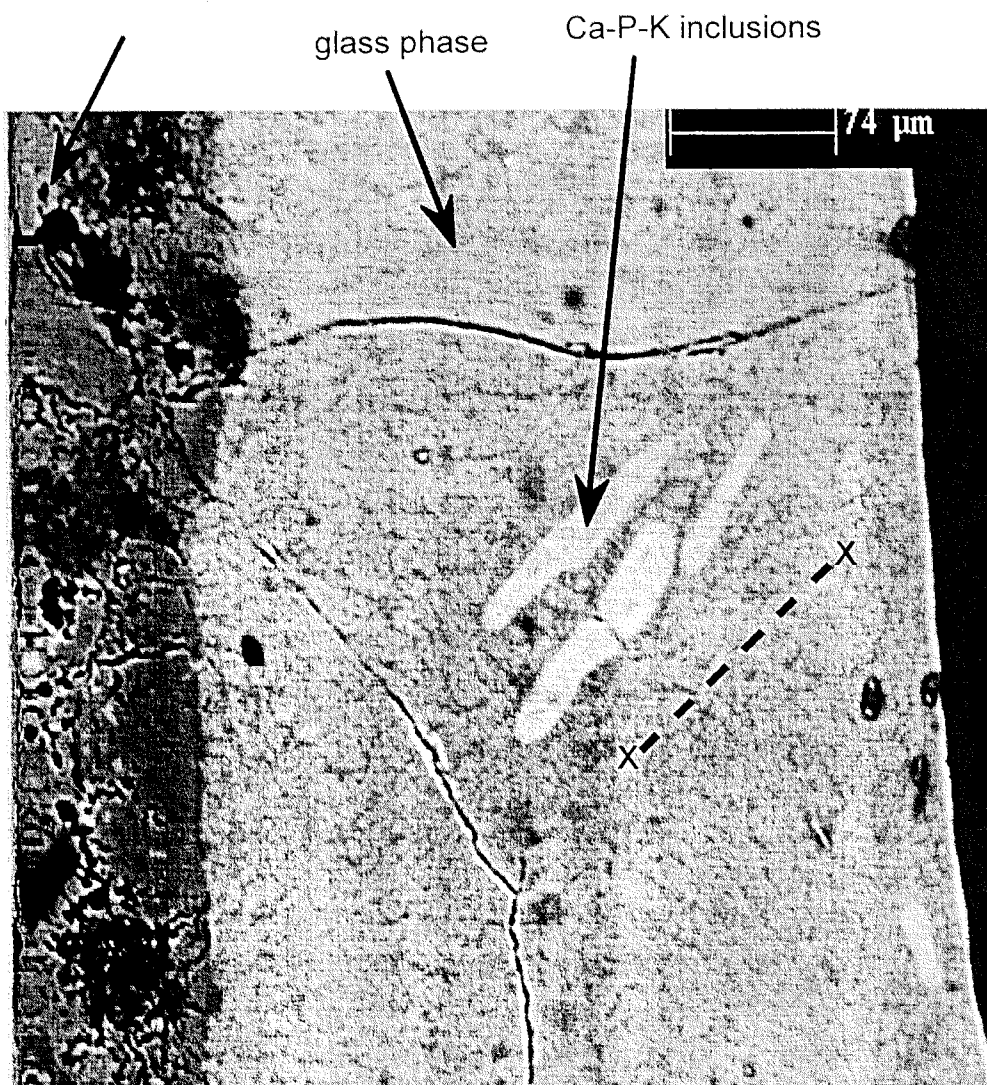


Figure 8. Backscattered electron image of slag from hardwood lignin, 225X. Dashed line X---X indicates line along which analyses of glass phase composition were collected. Also shown are apatite (calcium phosphate) inclusions.

**Table 6. Compositions of softwood and hardwood lignin slags.**

Oxide	Softwood Glass	Hardwood Glass	Hardwood Inclusions
SiO <sub>2</sub>	58.26	17.85	3.15
Al <sub>2</sub> O <sub>3</sub>	13.86	3.49	0.44
TiO <sub>2</sub>	0.94	0.26	0.03
Fe <sub>2</sub> O <sub>3</sub>	2.92	1.53	0.20
CaO	10.11	22.81	33.92
MgO	2.54	5.42	2.22
Na <sub>2</sub> O	6.33	1.56	2.29
K <sub>2</sub> O	2.08	16.88	15.85
P <sub>2</sub> O <sub>5</sub>	0.31	27.13	39.95
SO <sub>3</sub>	0.39	0.43	0.14
Total	97.74	97.36	98.19

apatitic glass, rich in calcium and phosphorous, as well as potassium. Apatite inclusions recrystallized from the melt are evident in the image of Figure 8. These are also associated with a high concentration of potassium (Table 6). The chemistry of the slags are substantially different, and imply different fouling responses if lignin is blended with other fuels during firing.

The softwood slag composition reveals that little elemental volatilization has occurred other than the release of sulfur. Comparison with the fuel ash composition of Table 1 shows all elements other than sulfur to have been largely retained in the melt, and nearly all sulfur is depleted in the glass. This result supports the nearly complete volatilization of sulfur at higher temperatures, a result consistent with the tube furnace experiments. The hardwood slag also reveals nearly complete volatilization of sulfur, but in contrast to the softwood results, potassium has also been volatilized, leading to the likely formation of potassium sulfate in deposits on boilers burning hardwood lignin. The retention of potassium in the softwood lignin is likely due to the higher silica concentration in the ash of this fuel.

## 5.0 Conclusions

The two lignin residues appear to be of low to moderate fouling type. Weak sintering was observed in the whole pellet fusibility test at 900° for the hardwood and 950°C for the softwood residue. The hardwood lignin contains substantially more alkali and has a higher total ash content compared to the softwood material. The alkali index for hardwood lignin indicates a greater propensity for fouling.

The hardwood lignin also contains more sulfur, possibly resulting from the acid pretreatment, even after washing. SO<sub>2</sub> release from hardwood lignin burned at 800°C was about 4 times greater than for softwood lignin, and in direct proportion to the total sulfur content of the fuels. Compositions of high temperature slags produced from the lignins reveal nearly complete sulfur volatilization, but the hardwood lignin also releases substantially greater potassium to the gas phase compared with the softwood lignin. The greater potassium volatilization likely would lead to greater potassium sulfate deposition on heat exchangers and other surfaces in boilers burning hardwood lignin.

Both lignins possessed very fine particle sizes after drying, and would require special handling for use as fuel in most power plants, except possibly suspension units. Larger scale tests of the combustion of these lignins should be conducted.

## 6.0 References

1. Himmel, M.E., J.O. Baker, R.P. Overend (1994). Enzymatic Conversion of Biomass for Fuel Production, ed. by M.J. Comstock, American Chemical Society, Washington, D.C.
2. Jenkins, B.M., L.L. Baxter, T.R. Miles Jr., T.R. Miles (1998). Combustion Properties of Biomass, Fuel Processing Technology, 54, pp. 17-46.
3. Richardson, B., A.P. Watkinson, P.V. Barr (1990). Combustion of Lignin in a Pilot Lime Kiln, Tappi Journal, 73, pp. 133-137.
4. Boye, D.M. Utilization of Lignins and Lignin Derivatives, Bib. Ser. No. 292, Inst. Of paper Chemistry, Appleton, WI. Abstract No. 1436, 1873, 1896, 2045, 3611, and 3703.
5. Yomogida, D. and B.M. Jenkins. (1997). Thermal Characteristics of Ligneous Residue from the Enzymatic Hydrolysis of Mixed Waste Feedstock, STEP-2 Feasibility Study of Ethanol Production From Biomass Residues in San Joaquin County, NREL, Golden, CO.
6. Yomogida, D. and B.M. Jenkins. (1997). Feasibility Study of Rice Straw-to-Ethanol in Gridley, California, Thermal Conversion Study, Stone & Webster Subcontract No. PS-026443, National Renewable Energy Laboratory Subcontract No. ZCG 6-15143-01.
7. Jenkins, B.M., R.R. Bakker, J.B. Wei. (1996). On the Properties of Washed Straw. Biomass and Bioenergy, 10(4):177-200.